room temperature for 15 min. The color of the dianion faded immediately on addition of the methyl iodide. The mixture was quenched with 2 ml of concentrated hydrochloric acid plus 5 ml of water and diluted with 15 ml of ethyl ether. The organic phase was washed with water until the aqueous extracts were neutral pH, dried over magnesium sulfate, and filtered. The solvents were removed under reduced pressure and the crude product was distilled to yield 1.06 g (81%) of methyl 3-oxovalerate.[9]

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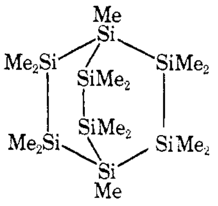
Cyclic Polysilanes. V. Tetradecylmethylbicyclo[2.2.2]octasilane, a Cage Polysilane[1]

Sir:

In continuing our studies of cyclic polysilanes, we have investigated the reaction of a mixture of Me_2SiCl_2 and $MeSiCl_3$ with sodium–potassium alloy. This reaction yields $Me_{14}Si_8$, the first fully characterized cage polysilane.[2,3]



Our assigned structure is based on spectral evidence. The exact molecular weight was determined by high-resolution mass spectrometry: calcd mass, 434.1440; found, 434.1439 ± 0.0043. The 100-MHz proton nmr taken in CCl_4 shows only two peaks, at −0.205 and −0.125 ppm (δ) with a relative intensity of 6:1, respectively.[4] The infrared spectrum of $Me_{14}Si_8$ is similar to those for the cyclosilanes $Me_{12}Si_6$ and $Me_{14}Si_7$ (Table I). It shows no absorption in the 3300-cm^{-1} or 1050-cm^{-1} region which would be indicative of Si–OH or Si–O–Si linkages, nor in the 2050–2300-cm^{-1} region characteristic of Si–H bonds. The ultraviolet spectrum in isooctane shows an inflection point at 245 nm (ϵ 7500). Tetradecylmethylbicyclo[2.2.2]octasilane is a white solid with mp >360°, but subliming readily at 100° and 0.3 Torr. It is air stable and soluble in organic solvents such as diethyl ether, chloroform, and carbon tetrachloride.

Table I. Infrared Spectra[a]

$Me_{14}Si_8$	$Me_{14}Si_7$	$Me_{12}Si_6$
2950 (s)	2950 (s)	2950 (s)
2890 (s)	2890 (m)	2885 (m)
2790 (w)	2790 (w)	2790 (w)
1400 (m)	1400 (m)	1400 (m)
1245 (s)	1250 (s)	1250 (s)
1240 (sh)	1240 (m)	1240 (m)
840 (m)	845 (m)	845 (m)
800 (vs)	830 (m)	830 (m)
725 (m)	795 (vs)	800 (vs)
685 (w)	735 (m)	735 (m)
670 (m)	690 (m)	690 (m)
650 (s)	655 (s)	655 (s)
630 (w)	630 (w)	630 (w)
390 (w)	362 (w)	383 (m)
375 (m)		

[a] Abbreviations used are: vs, very strong; s, strong; m, medium; w, weak; sh, shoulder.

In a typical experiment 20 ml (0.165 mol) of Me_2SiCl_2 and 20 ml (0.18 mol) of $MeSiCl_3$ in 40 ml of THF were added dropwise over 4 hr to 3 g (0.023 mol) of naphthalene and 0.95 mol of sodium–potassium alloy (27 g of potassium and 6 g of sodium) in 500 ml of dry THF. The reaction was mechanically stirred and kept at reflux (65°) during the chlorosilane addition. At the completion of the reaction, methanol and water were added to destroy the excess sodium–potassium alloy. The solution was then extracted with 400 ml of diethyl ether, and the organic layer was separated and vacuum distilled. The fraction boiling between 160 and 180° at 0.3 Torr was collected and purified by preparative gas chromatography,[5] yielding $Me_{14}Si_8$. The compound can be purified further by recrystallization from ether–acetone (1:1) or by vacuum sublimation at 100° and 0.3 Torr.

The yield of $Me_{14}Si_8$ is 0.5%, with residue (50%), siloxanes (44%), $Me_{12}Si_6$ (5%), and $Me_{18}Si_{10}$[6] (0.5%) accounting for the remainder.

The monocyclic permethylpolysilanes are reducible to electron-delocalized anion radicals, $(Me_2Si)_n\cdot^-$.[1] We find that $Me_{14}Si_8$ is similarly reduced by sodium–potassium alloy in glyme–methyl THF (2:1) solvent at −90° to give an anion radical observable by esr. Work is

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(1) Previous paper in this series: E. Carberry, R. West, and G. E. Glass, *J. Amer. Chem. Soc.*, **91**, 5446 (1969).

(2) The reactions

$$SiBr_4 + Si(metal) \xrightarrow{1150^\circ} Si_{10}Br_{16}$$

and

$$Si_{10}Br_{16} + CH_3MgI \xrightarrow{ether} (CH_3)_{16}Si_{10}$$

have been reported, but no structural data on $Si_{10}Br_{16}$ or $Me_{16}Si_{10}$ have been published: M. Schmeisser (a) IUPAC Colloquium (Münster 1954), Silicium-Schwefel-Phosphate 28, 1955; (b) *Angew. Chem.*, **66**, 713 (1954).

(3) V. G. Schatt and R. Nagel (*J. Prakt. Chem.*, [4] 34, 158 (1966)) have reported the existence of $(C_6H_5)_{10}Si_{10}Br_6$. The compound was obtained as a by-product of the reaction of phenyltribromosilane with phenylmagnesium bromide. It could not be crystallized and was characterized only by elemental analysis and molecular weight determination.

(4) The chemical shift of the MeSi protons in $Me_{14}Si_8$ follows the pattern observed in $(Me_3Si)_3SiMe$, where the protons of the MeSi are at higher field, −0.05 ppm (δ), than the protons of Me_3Si, −0.14 ppm (δ). W. H. Atwell and D. R. Weyenberg, *J. Organometal. Chem.*, **5**, 594 (1966).

(5) Good separation was obtained at 300° using a $^3/_8$ in. × 10 ft column packed with 20% Apiezon L on Chromosorb W, and a helium flow rate of 160 ml/min. Retention time for $Me_{14}Si_8$ was 12.5 min.

(6) $Me_{18}Si_{10}$ shows four peaks in the proton nmr, −0.14, −0.15, −0.19, and −0.255 ppm (δ) in the ratio of 2:2:1:4, respectively. The molecular weight was determined by high-resolution mass spectrometry; calcd mass, 550.1918; found, 550.1955 ± 0 0050. Its infrared spectrum is similar to those for $Me_{14}Si_8$ and the permethylated cyclopolysilanes. We suspect it to have either the decalin- or the bicyclo[3.3.2], or -[4.2.2] (suggested by the referee) decane-type structure. If the nmr cannot differentiate between the methyl groups syn and anti to the 4 bridge and 2 bridge in the bicyclo[4.2.2] and -[3.3.2], respectively, then four peaks, as observed, would appear in the nmr. However if the syn and anti positions are sufficiently different, then six peaks for the bicyclo[3.3.2] structure and five peaks for the bicyclo[4.2.2] structure should be observed. Likewise the decalin-type structure would exhibit three peaks if no distinction between the axial and equatorial methyl groups is observable, but five peaks if the difference in chemical shift is large enough. The nmr spectra were recorded on a Varian XL100-MHz instrument at a sweep width of 25 cycles.

currently in progress to determine if the esr signal observed is that of the parent anion $(Me_{14}Si_8)\cdot^-$.

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Deuteron Nuclear Magnetic Resonance Spectra of Some Paramagnetic Transition Metal Acetylacetonates

Sir:

Isotropic nmr shifts have proven to be extremely useful for investigating a number of solution properties of paramagnetic transition metal complexes, such as bonding, kinetics and thermodynamics of stereochemical equilibria, and isomerism.[1,2] Unfortunately, well-resolved spectra are realized for only a limited number of metal ions, since a rapid electron spin relaxation time, τ_s, is required. In 1965, Eaton[3] measured pmr line widths of a series of transition metal acetylacetonate complexes in an effort to determine which ions have sufficiently short τ_s's for useful pmr studies. The best resolution was found for acetylacetonates of V(III), Mn(III), and Ru(III). Well-resolved spectra have been observed for certain complexes of other ions, notably Ni(II), Co(II), and Cr(II).[1,2] It appears that τ_s is a function of ligand-field strength and symmetry.

Recently Reuben and Fiat[4] pointed out that deuteron nmr (dmr) signals in a paramagnetic environment should be narrower than pmr signals under the same conditions by a factor of $\gamma_H{}^2/\gamma_D{}^2 = 42.5$, where γ_H and γ_D are the magnetogyric ratios of the proton and deuteron. Since chemical shift differences in hertz are smaller for dmr by a factor of $\gamma_H/\gamma_D = 6.5$, the overall resolution of the dmr spectrum should be better by a factor of 6.5.[5] The only dmr studies of paramagnetic systems reported thus far have involved solutions of metal ions in deuterium oxide.[6]

We have examined dmr spectra of six deuterium-substituted, paramagnetic acetylacetonate complexes in order to compare the resolution of dmr and pmr for discrete molecular species. Pmr spectra of the corresponding protonated complexes were also recorded in order to make line-width comparisons under the same conditions. Proton and deuteron spectra were run at 100 and 15.3 MHz, respectively, using a Varian HA-100 instrument. Deuterium-substituted acetylacetone was prepared by refluxing acetylacetone in D_2O with a small amount of Na_2CO_3. The complexes were prepared by methods described in the literature.[7] Chemical shift values *in parts per million* of the isotropically shifted resonances are in agreement with those reported by Eaton[3] and are the same for the pmr and dmr spectra of a given complex, since isotropic shifts are independent of the nuclear magnetogyric ratio.[8] The line widths measured in hertz at half maximum amplitude are given in Table I.

Table I. Comparison of Pmr and Dmr Line Widths[a,b]

Complex	Pmr line width, *A*,[c] Hz	Dmr line width, *B*,[c] Hz	Ratio *A*/*B*
$V(acac)_3$	46	2.6[d]	~18
$Cr(acac)_3$	1400	35	40
$Mo(acac)_3$	310	18[d]	~17
$Mn(acac)_3$	96	10	~10
$Fe(acac)_3$	920	36	26
$Ru(acac)_3$	35	3.9	~9

[a] In $CDCl_3$ solution at 30°. [b] Error estimates are in the range 3–10%. [c] Data refer to the methyl resonance. [d] Value obtained from one component of multiplet (see text).

The methyl dmr resonance of the deuterated V(III) complex surprisingly appeared as a multiplet of three signals with separations of the order of 8–10 Hz. The ligand used to prepare this complex was deuterated only to an extent of ~80%. Thus *pmr* of the same sample was feasible and showed an identical multiplet with separations of ~55 Hz. The complex was prepared again using ligand >90% deuterated. Dmr and pmr of this sample showed a dominant peak accompanied by a small satellite at higher field.[9] Multiple dmr signals were also found for the Mo(III) complex. It appears that chemical shift differences are so magnified by the isotropic shift effect that complexes differing only in the extent of deuterium substitution are distinguishable. The phenomenon will be further investigated.

The Solomon–Bloembergen expressions for the longitudinal and transverse relaxation times of nuclei in a paramagnetic molecule contain a number of variables, including the electron–nuclear distance, the electron relaxation time, the electron Larmor frequency, the tumbling time of the molecule, and the square of the nuclear magnetogyric ratio, γ_N.[10] Upon replacing a proton by a deuteron in a given molecule, the only

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(1) (a) D. R. Eaton and W. D. Phillips, *Advan. Magn. Resonance*, **1**, 103 (1965); (b) E. de Boer and H. van Willigen, *Progr. Nucl. Magn. Resonance Spectrosc.*, **2**, 111 (1967); (c) R. H. Holm, *Accounts Chem. Res.*, **2**, 307 (1969).

(2) (a) L. H. Pignolet, W. DeW. Horrocks, Jr., and R. H. Holm, *J. Amer. Chem. Soc.*, **92**, 1855 (1970); (b) G. N. La Mar and E. O. Sherman, *ibid.*, **92**, 2691 (1970); (c) G. N. La Mar, *ibid.*, **92**, 1806 (1970); (d) G. N. La Mar and G. R. Van Hecke, *ibid.*, **92**, 3021 (1970); (e) R. E. De Simone and R. S. Drago, *ibid.*, **92**, 2343 (1970), and references cited in these papers.

(3) D. R. Eaton, *ibid.*, **87**, 3097 (1965).

(4) J. Reuben and D. Fiat, *ibid.*, **91**, 1242 (1969).

(5) This factor does not take into account the lower signal-to-noise ratio and quadrupolar broadening for dmr. Quadrupolar broadening is expected to be masked by the more efficient magnetic dipole relaxation mechanism in a paramagnetic environment.[6a]

(6) (a) G. Laukien and F. Noack, *Z. Phys.*, **159**, 311 (1960); (b) P. Diehl and T. Leipert, *Helv. Chim. Acta*, **47**, 545 (1964).

(7) $V(acac)_3$, G. W. Everett, Jr., and Y. T. Chen, *J. Amer. Chem. Soc.*, **92**, 508 (1970); $Cr(acac)_3$, W. C. Fernelius and J. E. Blanch, *Inorg. Syn.*, **5**, 130 (1957); $Mo(acac)_3$, M. L. Larson and F. W. Moore, *ibid.*, **8**, 153 (1964); $Mn(acac)_3$, R. G. Charles, *ibid.*, **7**, 183 (1963); $Fe(acac)_3$, A. Hantzsch and C. H. Desch, *Justus Liebigs Ann. Chem.*, **323**, 1 (1902); $Ru(acac)_3$, G. A. Barbieri, *Atti Accad. Lincei Rend.*, **23**, 334 (1914).

(8) The contact contribution to the isotropic shift is given[1] as $(\Delta H/H_0)_i = -A_i(\gamma_e/\gamma_N)(g\beta S(S+1)/3kT)$. Since the coupling constant A_i is proportional to γ_N, $\Delta H/H_0$ is independent of γ_N. The expression for the dipolar contribution does not contain γ_N.[1a]

(9) Since this communication was submitted we have prepared 100%-deuterated ligand. A single methyl resonance is observed for the V(III) complex of this ligand.

(10) For a discussion of these equations, see R. A. Bernheim, T. H. Brown, H. S. Gutowsky, and D. E. Woessner, *J. Chem. Phys.*, **30**, 950 (1959).